

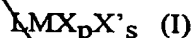
CLAIMS

1. A multi-stage process for the polymerization of olefins comprising:
- (I) a first polymerization stage, wherein one or more olefins of formula $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{10}$ alkyl, cycloalkyl or aryl radical, are polymerized in one or more reactors, in the presence of a catalyst comprising the product of the reaction between an alkyl-Al compound and a solid component comprising at least one compound of a transition metal M^{I} chosen between Ti and V, and not containing $\text{M}^{\text{I}}\text{-}\pi$ bonds, and a halide of Mg, in order to produce an olefinic polymer having porosity, expressed as percentage of voids, greater than 5%;
- (II) a treatment stage, wherein the product obtained in said first polymerization stage (I) is, in any order whatever:
- (a) optionally contacted with a compound capable of deactivating the catalyst used in stage (I); and
- (b) contacted with a late transition metal complex, optionally in the presence of a suitable activating agent; and
- (III) a second polymerization stage, wherein one or more olefinic monomers are polymerized in one or more reactors, in the presence of the product obtained from stage (II).
2. The multi-stage process according to claim 1 wherein, in stage (I), said alkyl-Al compound is a trialkyl-Al, an alkyl-Al halide or an alkyl-Al sesquichloride, said halide of Mg is MgCl_2 and said compound of a transition metal M^{I} is selected from the group consisting of halides of Ti, halo alkoxides of Ti, VCl_3 , VCl_4 , VOCl_3 and halo alkoxides of V.
3. The multi-stage process according to claim 2, wherein said compound of a transition metal M^{I} is selected from the group consisting of TiCl_4 , TiCl_3 and halo alkoxides of the formula $\text{Ti}(\text{OR}^{\text{I}})_m\text{X}_n$, wherein R^{I} is a $\text{C}_1\text{-C}_{12}$ hydrocarbon radical or a $-\text{COR}^{\text{I}}$ group, X is halogen and $(m+n)$ corresponds to the oxidation state of Ti.
4. The multi-stage process according to claim 1 wherein, in stage (I), said solid component is in the form of spherical particles having a mean diameter ranging from 10 μm to 150 μm .
5. The multi-stage process according to claim 1, wherein the catalyst used in stage (I) comprises the product of the reaction between an Al-alkyl compound, an electron-donating compound (external donor) and a solid component comprising at least one compound of a transition metal M^{I} selected from Ti and V and not containing $\text{M}^{\text{I}}\text{-}\pi$ bonds, a magnesium halide and an

electron-donating compound (internal donor).

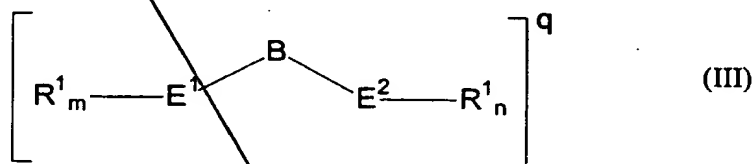
6. The multi-stage process according to claim 1, wherein the porosity of the olefinic polymer obtained in the first polymerization stage (I) is greater than 10%.
7. The multi-stage process according to claim 6, wherein more than 40% of said porosity is due to pores with diameter greater than 10,000 Å.
8. The multi-stage process according to claim 1 wherein, in the treatment stage (II)(a), said compound capable of deactivating the catalyst used in stage (I) has formula R^{IV}_yX , wherein R^{IV} is hydrogen or a C₁-C₁₀ hydrocarbon radical, X is O, N, or S, and y corresponds to the valence of X.
9. The multi-stage process according to claim 8, wherein said compound capable of deactivating the catalyst used in stage (I) is selected from the group consisting of H₂O, NH₃, H₂S, CO, COS, CS₂, CO₂ and O₂.

10. The multi-stage process according to claim 1 wherein, in the treatment stage (II)(b), said late transition metal complex has formula (I) or (II):



wherein M is a metal belonging to Group 8, 9, 10 or 11 of the Periodic Table;

L is a bidentate or tridentate ligand of formula (III):



wherein:

B is a C₁-C₅₀ bridging group linking E¹ and E², optionally containing one or more atoms belonging to Groups 13-17 of the Periodic Table;

E¹ and E², the same or different from each other, are elements belonging to Group 15 or 16 of the Periodic Table and are bonded to said metal M;

the substituents R¹, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₁-C₂₀ alkyliden, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table of the Elements (such as B, Al, Si, Ge, N, P, O, S, F and Cl atoms); or two R¹ substituents attached to the same atom E¹ or E² form a saturated, unsaturated or aromatic C₄-C₈ ring, having from 4 to 20 carbon atoms;

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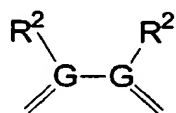
m and n are independently 0, 1 or 2, depending on the valence of E^1 and E^2 , so to satisfy the valence number of E^1 and E^2 ; q is the charge of the bidentate or tridentate ligand so that the oxidation state of $MX_pX'_s$ or MA is satisfied, and the compound (I) or (II) is overall neutral; X , the same or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, $-R$, $-OR$, $-OSO_2CF_3$, $-OCOR$, $-SR$, $-NR_2$ and $-PR_2$ groups, wherein the R substituents are linear or branched, saturated or unsaturated, C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table of the Elements (new IUPAC notation), such as B, N, P, Al, Si, Ge, O, S and F atoms; or two X groups form a metallacycle ring containing from 3 to 20 carbon atoms; the substituents X are preferably the same;

X' is a coordinating ligand selected from mono-olefins and neutral Lewis bases wherein the coordinating atom is N, P, O or S;

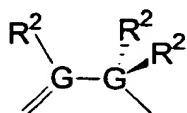
p is an integer ranging from 0 to 3, so that the final compound (I) or (II) is overall neutral;

s ranges from 0 to 3; and A is a π -allyl or a π -benzyl group.

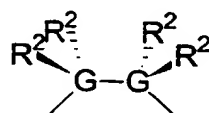
11. The multi-stage process according to claim 10, wherein said bridging group B is selected from the group consisting of:



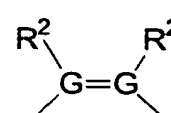
B-1



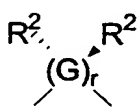
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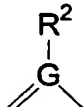
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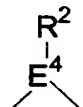
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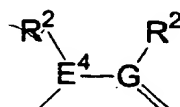
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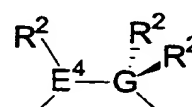
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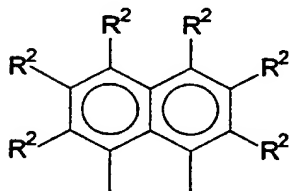
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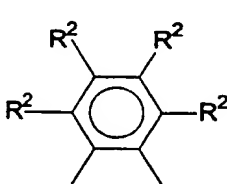
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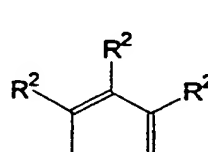
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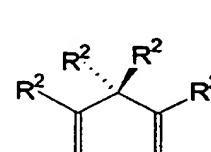
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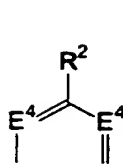
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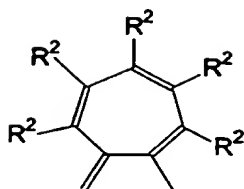
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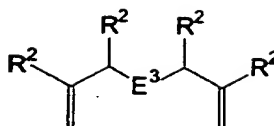
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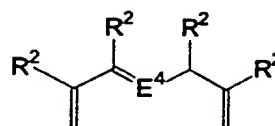
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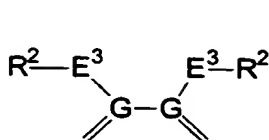
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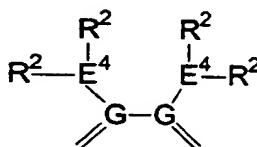
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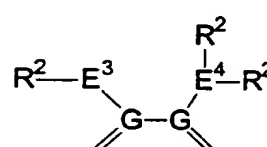
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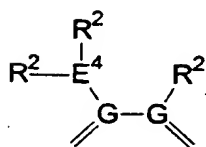
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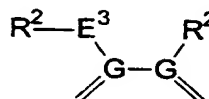
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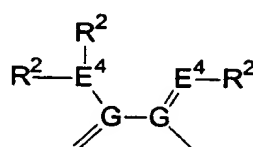
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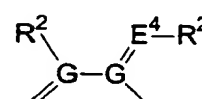
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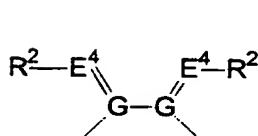
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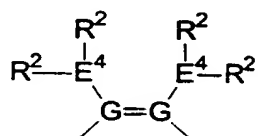
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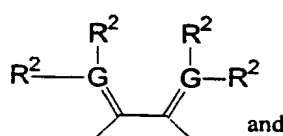
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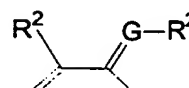


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and



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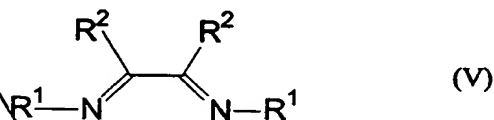
wherein G is an element belonging to Group 14 of the Periodic Table; r is an integer ranging from 1 to 5; E³ is an element belonging to Group 16 and E⁴ is an element belonging to Group 13 or 15 of the Periodic Table; the substituents R², the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₁-C₂₀ alkoxy, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; or two R² substituents form a saturated, unsaturated or aromatic C₄-C₈ ring, having from 4 to 20 carbon atoms, or they form a polycyclic ring system, optionally containing one or more Group 13-16 elements; a substituent R¹ and a substituent R² may form a substituted or unsubstituted, saturated, unsaturated or aromatic

C₄-C₈ ring, having from 4 to 20 carbon atoms and optionally containing one or more Group 13-16 element.

12. The multi-stage process according to claim 10, wherein E¹ and E² are selected from the group consisting of N, P, O, and S.

13. The multi-stage process according to claim 10, wherein the substituents R¹ are C₆-C₂₀ aryl groups; the substituents X are selected from the group consisting of hydrogen, methyl, phenyl, Cl, Br and I; and p is 1, 2 or 3.

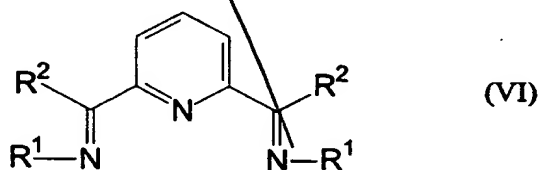
14. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (V):



wherein R¹ and R² have the meaning reported in claims 10 and 11; M belongs to Group 10 of the Periodic Table; X radicals are hydrogen, methyl, Cl, Br or I; p is 2 or 3; and s is 0.

15. The multi-stage process according to claim 14, wherein the substituents R¹ are C₆-C₂₀ aryl groups, optionally substituted in the 2 and 6 positions with alkyl groups containing 1 to 20 carbon atoms and/or halo groups; the substituents R² are selected from the group consisting of hydrogen, methyl, ethyl, n-propyl, i-propyl and benzyl, or the two substituents R² form together an acenaphtenquinone group.

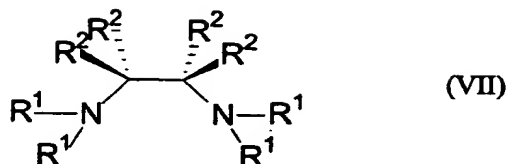
16. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (VI):



wherein the R¹ and R² groups have the meaning reported in claims 10 and 11, the metal M is Fe or Co; the X radicals are preferably hydrogen, methyl, Cl Br or I; p is 2 or 3; and s is 0.

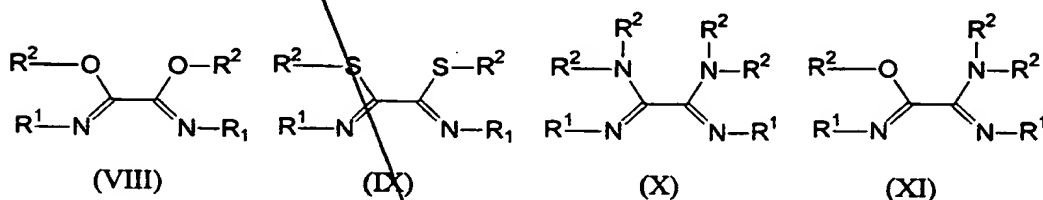
17. The multi-stage process according to claim 16, wherein the substituents R^2 are hydrogen or methyl, and the substituents R^1 are aryl rings.

18. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (VII):



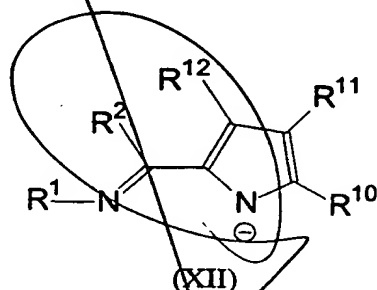
wherein R^1 and R^2 have the meaning reported in claims 10 and 11, M belongs to group 10 of the Periodic Table, the X radicals are hydrogen, methyl, Cl, Br or I; p is 2 or 3; and s is 0.

19. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to one of formulae (VIII)-(XI):



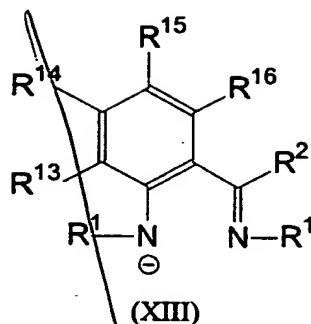
wherein R^1 and R^2 have the meaning reported in claims 10 and 11, M belongs to Group 10 of the Periodic Table, the X radicals are hydrogen, methyl, Cl, Br or I; p is 2 or 3; and s is 0.

20. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XII):



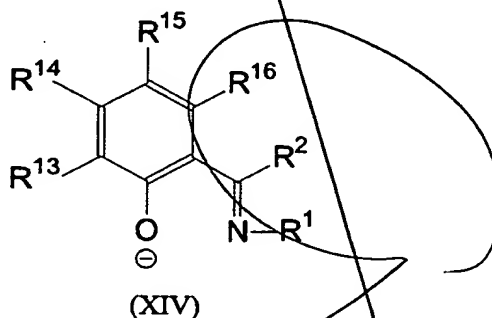
wherein R^1 and R^2 have the meaning reported in claims 10 and 11; R^{10} - R^{12} , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl and C_7 - C_{20} arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; or two adjacent substituents R^{10} - R^{12} form a saturated, unsaturated or aromatic C_4 - C_8 ring, having from 4 to 40 carbon atoms; the metal M is preferably Fe, Co, Rh, Ni or Pd; the X radicals are hydrogen, methyl, Cl Br or I; p is 2 or 3; and s is 0.

21. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XIII):



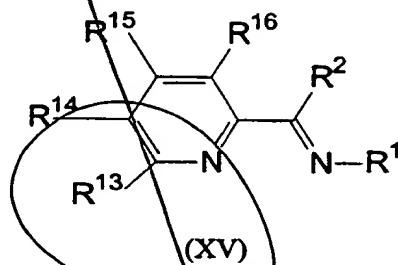
wherein R^1 and R^2 have the meaning reported in claims 10 and 11; the substituents R^{14} and R^{16} , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl and C_7 - C_{20} arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; the substituents R^{13} and R^{15} , the same or different from each other, have the same meaning of substituents R^{14} and R^{16} , optionally forming with an adjacent substituent R^{14} or R^{16} a saturated, unsaturated or aromatic C_4 - C_8 ring, or they are electron withdrawing groups; the metal M is Fe, Co, Ni or Pd; the X radicals are hydrogen, methyl, Cl Br or I; p is 2 or 3; and s is 0.

22. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XIV):



wherein R^1 and R^2 have the meaning reported in claims 10 and 11; R^{14} and R^{16} , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl and C_7 - C_{20} arylalkyl radical, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; R^{13} and R^{15} , the same or different from each other, have the same meaning of R^{14} and R^{16} , optionally forming with an adjacent R^{14} or R^{16} a saturated, unsaturated or aromatic C_4 - C_8 ring, or they are electron withdrawing groups; the metal M belongs to Group 10 of the Periodic Table, the X radicals are hydrogen, methyl,

- allyl, Cl, Br or I, A is a C₃-C₅ linear allyl, p is 1 and s is 1.
23. The multi-stage process according to claim 22 wherein, in said ligand of formula (XIV), R¹ is aryl, substituted in the 2, 6 and/or 4 positions with a substituent selected from halogen and linear or branched C₁-C₂₀ alkyl groups, or is a tertiary C₃-C₆ alkyl group; R² is hydrogen or methyl; R¹⁴ and R¹⁶ are hydrogen, methyl or methoxy; R¹³ is selected from the group consisting of aryl, substituted in the 2 and 6 positions with branched C₃-C₃₀ alkyl groups, tertiary C₃-C₆ alkyl group, -NO₂ and halo; and R¹⁵ is selected from the group consisting of aryl, tertiary C₃-C₆ alkyl group, -NO₂, halo, -CF₃, -SO₃⁻, -SO₂R and -COO⁻.
24. The multi-stage process according to claims 10 and 11, wherein said ligand L corresponds to formula (XV):



- wherein R¹ and R² have the meaning reported in claims 10 and 11; the substituents R¹⁴ and R¹⁶, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl radicals, optionally containing one or more atoms belonging to groups 13-17 of the Periodic Table; the substituents R¹³ and R¹⁵, the same or different from each other, have the same meaning of substituents R¹⁴ and R¹⁶, optionally forming with an adjacent substituent R¹⁴ or R¹⁶ a saturated, unsaturated or aromatic C₄-C₈ ring, or they are electron withdrawing groups; the metal M belongs to Group 10 of the Periodic Table; the X radicals are hydrogen, methyl, Cl, Br or I, p is 2 or 3, s is 0.
25. The multi-stage process according to claim 1 wherein, in the treatment stage (II)(b), said activating agent is an alumoxane and/or a compound able to form an alkylmetal cation.
26. The multi stage process according to claim 1 wherein, in the treatment stage (II), the product obtained in the first polymerization stage (I) is, in the following order:
- (a) first contacted with said compound capable of deactivating the catalyst used in stage (I); and
 - (b) then contacted with said late transition metal complex, optionally in the presence of a suitable activating agent.
27. The multi-stage process according to claim 26 wherein, before step (b), any excess of said

- compound capable of deactivating the catalyst used in stage (I) is removed.
28. The multi-stage process according to claim 1, wherein the polymerization stage (I) is carried out in liquid phase, said liquid phase consisting of a hydrocarbon solvent or of one or more olefins $\text{CH}_2=\text{CHR}$, and the polymerization stage (III) is carried out in gas phase, in at least one reactor with a fluidized bed or a mechanically-agitated bed.
 29. The multi-stage process according to claim 1, wherein both polymerization stages (I) and (III) are carried out in gas phase, in reactors with a fluidized bed or a mechanically-agitated bed.
 30. A catalyst component for the polymerization of olefins comprising a late transition metal complex supported on a polymeric porous support having a porosity, expressed as percentage of voids, greater than 5%.
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31. A catalyst component for the polymerization of olefins comprising a late transition metal complex supported on a polymeric porous support having a porosity, expressed as percentage of voids, greater than 5%, said catalyst component being obtainable by a process comprising:
 - (I) a polymerization stage, wherein one or more olefins of formula $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{10}$ alkyl, cycloalkyl or aryl radical, in the presence of a catalyst comprising the product of the reaction between one or more alkyl-Al compounds and a solid component comprising at least one compound of a transition metal M^{I} chosen between Ti and V, and not containing $\text{M}^{\text{I}}\text{-}\pi$ bonds, and a halide of Mg;
 - (II) a treatment stage, wherein the product obtained in the polymerization stage (I) is, in any order whatever:
 - (a) optionally contacted with one or more compounds capable of deactivating the catalyst used in step (I); and
 - (b) contacted with one or more late transition metal complexes, optionally in the presence of a suitable activating agent.
 32. The catalyst component according to claim 30 or 31, wherein said late transition metal complex is supported in a quantity ranging from 1.10^{-7} to 1.10^{-1} mmol per gram of polymeric porous support.
 33. The catalyst component according to claim 30 or 31, wherein said polymeric porous support has a porosity greater than 10%.
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34. The catalyst component according to claim 33, wherein more than 40% of the porosity is due to pores with diameter greater than 10,000 Å.
 35. A polymer composition obtainable with the process of claim 1, characterized in that:

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- in said first polymerization stage a homo or copolymer of propylene is obtained, having a content of propylene units greater than 80% wt. and cold xylene soluble fractions lesser than 40% wt., said homo or copolymer of propylene consisting of 10-90 %wt. of the total amount of polymer; and
 - in said second polymerization stage amorphous polyethylene is produced, having a number of total branching greater than 50 branches/1000 C, a density ranging from 0.830 and 0.880 g/cm², and a Tg value lesser than -30°C.

36. A polymer composition obtainable with the process of claim 1, characterized in that:

- in said first polymerization stage polyethylene, polypropylene or propylene/ethylene copolymer is produced, consisting of 10-90 %wt. of the total amount of polymer; and
- in said second polymerization stage block polyethylene is produced, having a melting point ranging from 100 to 130°C and a Tg value lesser than -30°C.

37. A polymer composition obtainable with the process of claim 1, characterized in that:

- in said first polymerization stage, a copolymer of ethylene with one or more α -olefins (LLDPE) is obtained, having a content of ethylene units of 80-99%wt., said copolymer of ethylene consisting of 10-90 %wt. of the total amount of polymer;
 - in the second polymerization stage, polyethylene is produced having a number of total branching greater than 5 branches/1000 C and a density greater than 0.880 g/cm³.
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